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RESEARCH IN ENERGETIC COMPOUNDS

A Report on Work Sponsored by the
OFFICE OF NAVAL RESEARCH

Contract N00014-88-C-0536
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October 1989

FLUOROCHEM, INC.

680 South Ayon Avenue
Azusa, California 91702

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by

R. D. Chapman, T. G. Archibald and K. Baum

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19. ABSTRACT

The synthesis of cyclic compounds containing difluoramino and nitro groups was investigated. The Mannich reaction of 2-bromo-2-nitro-1,3-propanediol with *t*-butylamine yielded 2-bromo-*N,N'*-di-*tert*-butyl-2-nitro-1,3-propanediamine. Cyclization of this diamine with formaldehyde, followed by nitrolysis with 100% nitric acid, yielded 5-bromohexahydro-1,3,5-trinitropyrimidine, a potential precursor to 5,5-bis(difluoramino)hexahydro-1,3-dinitropyrimidine.

1,5-Dibenzyloctahydro-3,7-bis(methylene)-1,5-diazocine, obtained by the alkylation of *N,N'*-dibenzyl-2-methylene-1,3-propanediamine with 3-iodo-2-iodomethylpropene, was debenzylated with 1-chloroethyl chloroformate. The resulting secondary amine, octahydro-3,7-bis(methylene)-1,5-diazocine, was acetylated to give 1,5-diacetyloctahydro-3,7-bis-(methylene)-1,5-diazocine. Ozonolysis yielded the corresponding diketone, 1,5-diacetyltetrahydro-1,5-diazocine-3,7(2*H*,6*H*)-dione, which was converted to the dioxime. Although nitration of the dioxime with nitric acid, followed by hydrogen peroxide oxidation, yielded only a transannularly bridged bicyclic derivative, evidence for a *gem*-dinitro ketone was obtained when nitric acid-ammonium nitrate was used as the nitrating agent.

A new transformation of *gem*-dinitro to mononitro substituents, using N-benzyl-1,4-dihydronicotinamide, was demonstrated by the quantitative conversion of 2,2-dinitropropane to 2-nitropropane. This reagent, however, was also found to denitrate nitramines, preventing its utilization for the selective denitration of a *gem*-dinitro group in octahydro-1,3,3,5,7,7-hexanitro-1,5-diazocine (HNDZ).

Attempts to oxidize 3,3-dinitrocyclobutanol to 3,3-dinitrocyclobutanone were unsuccessful. Initial attempts to prepare 1-acetyl-3,5-piperidinedione were unsuccessful, yielding instead the *O*-acetylated enol acetate.

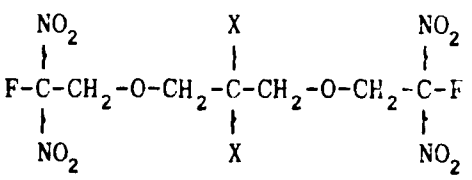
CONTENTS

INTRODUCTION

This report summarizes research under Contract N00014-88-C-0536 during the period 12 September 1988 through 11 September 1989. This work has emphasized the synthesis of new energetic compounds containing both difluoramino and nitro groups.

During the 1960's, extensive research was supported on the synthesis of difluoramino compounds, with some incidental work on mixed nitro-difluoramino compounds. Emphasis was placed on the development of propellants rather than explosives. Although the difluoramino group is a potent oxidizing functional group, a problem in its utilization in explosives results from the fact that performance in this application is strongly related to oxygen balance. Univalent fluorine is half as effective as divalent oxygen in providing a stoichiometric combustion balance. Also, compounds with a high percentage of difluoramino groups are relatively sensitive to impact. These problems are minimized if only a few difluoramino groups, compared to nitro groups, are incorporated into a target molecule.

The effect is seen by comparing the properties[1] of SYEP and FDNA, two compounds, prepared at Fluorochem in the 1970's, that differ only in that two nitro groups are replaced with difluoramino groups. Thus, despite a loss of "oxygen balance" for SYEP compared to FDNA, there is a substantial increase in detonation pressure, accompanied by only a small increase in impact sensitivity.

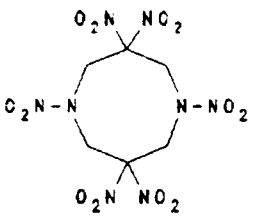


	SYEP ($X = NF_2$)	FDNA ($X = NO_2$)
mp (°C)	-2.5	21
Density (g cm^{-3})	1.691	1.640
I_{sp} (sec)	264.9	254.5
Detonation Pressure (Kbar)	273.75	249.05
Impact Sensitivity (cm/2.5 kg)	141	158

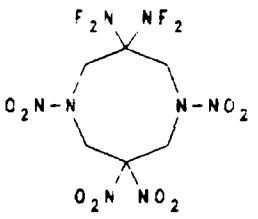
Recent advances that have been made in the synthesis of dense, cyclic explosives containing *gem*-dinitro and nitramino groups can be applied to the synthesis of related materials containing difluoramino groups. Difluoramino groups can be introduced into complex organic molecules by the reaction of carbonyl compounds (or their functional equivalents, such as *gem*-halonitro derivatives) with difluoramine in fuming sulfuric acid (difluorosulfamic acid).[2] Difluoramine is generated by the hydrolysis of *N,N*-difluorourea, prepared by the direct aqueous fluorination of urea.[3]

DISCUSSION

One of the target compounds on this program is 3,3-bis(difluoramino)-octahydro-1,5,7,7-tetranitro-1,5-diazocine, which is the difluoramino analogue of octahydro-1,3,3,5,7,7-hexanitro-1,5-diazocine, HNDZ.[4] Although the condensation chemistry that has led to HNDZ will be of utility for the synthesis of the difluoramino derivative, important differences derive from the asymmetry of the latter. Selective functionalization or stepwise build-up may be required.



HNDZ

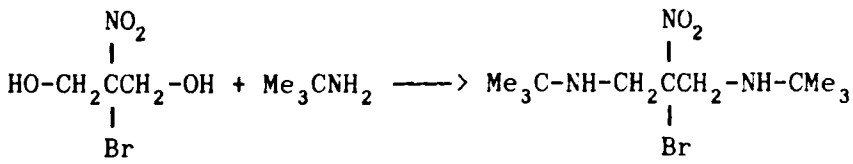


Condensations of 1-nitrobutane or 1-nitropropane with ammonia and formaldehyde were reported to produce octahydro-3,7-dinitro-3,7-dipropyl-1,5-diazocine or the analogous 3,7-diethyl derivative in low yield.[5] Since smaller nitroalkanes did not produce diazocine derivatives, bulky substituents may be required. In an attempt to apply this reaction, 2-nitroethanol was protected as the tetrahydropyranyl ether and then methylolated to the mono-THP ether of tris(hydroxymethyl)nitromethane. However, the Mannich reaction of this compound with ammonia did not yield any resolvable products, and nitration of the crude product did not give an isolable nitramine derivative. The *t*-butyldimethylsilyl ether of 2-nitroethanol behaved similarly.

Attempted condensations of 2-bromo-2-nitro-1,3-propanediol with ammonia or *t*-butylamine and of 2-chloro-2-nitro-1-butanol with morpholine also were unsuccessful under typical Mannich conditions. Reactions were conducted in water or methanol from room temperature to 80°C, with pH 5 to 8.

Mannich reactions run under unusual conditions using neat reactants, with a 2-halo-2-nitro-1,3-propanediol in the liquid amine as the solvent, have been reported by Senkus to yield the corresponding diamines;[6] 2-chloro-2-nitro-1,3-propanediol reacted with benzylamine to yield *N,N'*-dibenzyl-2-chloro-2-nitro-1,3-propanediamine. We applied these conditions to the reaction of 2-bromo-2-nitro-1,3-propanediol with *t*-butylamine and obtained 2-bromo-*N,N'*-di-

tert-butyl-2-nitro-1,3-propanediamine in 56% yield. In 1,1,2-trichlorotrifluoroethane (Freon-113) as solvent, the yield was improved to 89%.

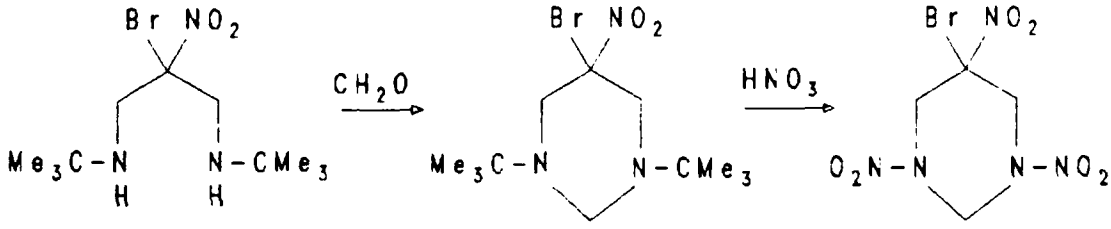


Attempts to extend this reaction to obtain a diazocine derivative with additional bromonitropropanediol were unsuccessful. Alkylations of *N,N'*-dialkyl-1,3-propanediamines with 1,3-dibromopropane have been reported to form 1,5-diazocines,[7,8] but 2-bromo-*N,N'*-di-*tert*-butyl-2-nitro-1,3-propanediamine gave only degradation products under the reported conditions. The reaction of 2-bromo-2-nitro-1,3-propanediol with 1,3-propanediamine gave water-soluble tars after an exothermic reaction. Excess 2-bromo-2-nitro-1,3-propanediol with *t*-butylamine yielded only 3-(*N*-*tert*-butylamino)-2-bromo-2-nitro-1-propanol. Attempts to condense 2,2-dinitro-1,3-propanediol (A-diol) with neat *t*-butylamine yielded only zwitterionic *N*-(2,2-dinitroethyl)-*t*-butylamine.[9] Attempts to cyclize the above bromo-nitro diamine with A-diol, and to nitrate the crude product, were also unsuccessful.

Cyclization of 2-bromo-*N,N'*-di-*tert*-butyl-2-nitro-1,3-propanediamine to a six-membered ring was accomplished with formaldehyde. The reaction with paraformaldehyde in methanol at room temperature for 3 days gave 5-bromo-1,3-di-*tert*-butylhexahydro-5-nitropyrimidine in 74% yield. The conditions reported for similar cyclizations,[10] formaldehyde in refluxing methanol or ethanol, resulted in degradation of the diamine reactant. An analogous compound, 5-chlorohexahydro-5-nitro-1,3-diisopropylpyrimidine, was previously

made by the chlorination of the nitronate salt of hexahydro-5-nitro-1,3-diisopropylpyrimidine, prepared from nitromethane, isopropylamine, and formaldehyde.[11]

The nitrolysis of 5-bromo-1,3-di-*tert*-butylhexahydro-5-nitropyrimidine with 100% HNO_3 at room temperature gave the corresponding nitramine in 43% yield. This compound will serve as a model reactant for the difluoramination of halonitro groups β to nitramines. The *gem*-dinitro analogue of the expected product, hexahydro-1,3,5,5-tetranitropyrimidine (DNNC), has been reported[11-13] and presents a standard of comparison for performance.



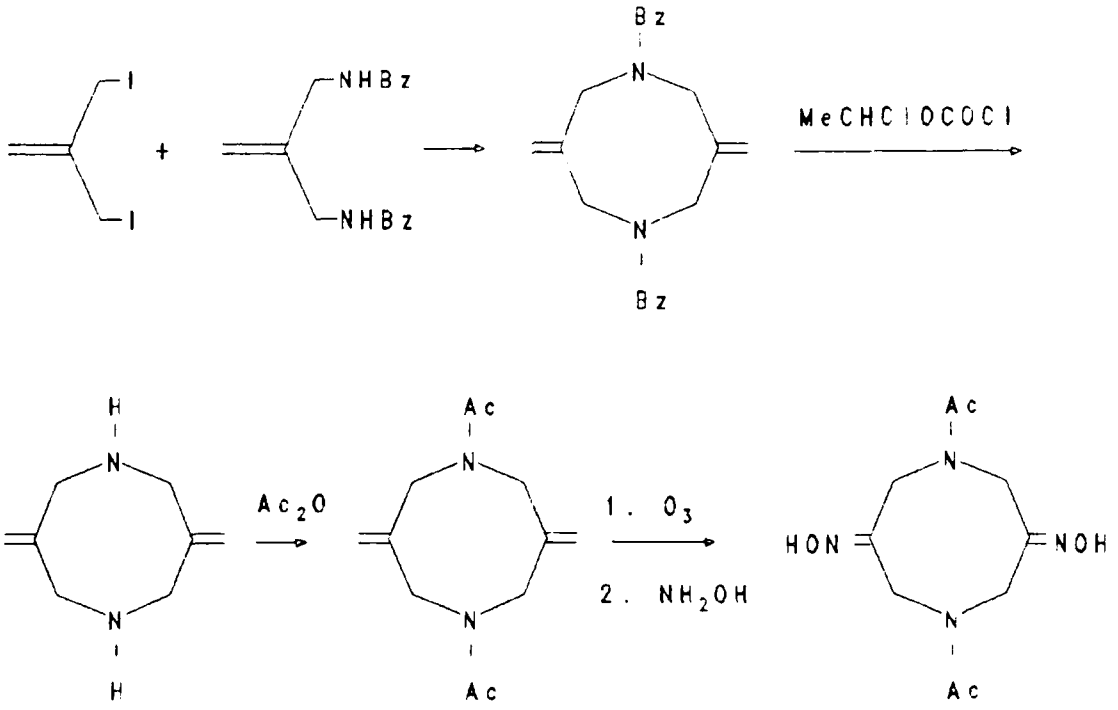
Another approach to difluoramino diazocine derivatives is selective replacement of a *gem*-dinitro group in the known analogue, HNDZ.[4] The reagent *N*-benzyl-1,4-dihydronicotinamide (BNAH) has been reported to effect a nitro-to-hydrogen conversion in α-nitro nitriles, esters, and ketones,[14] but a similar conversion in *gem*-dinitro compounds has not been reported. NMR analysis showed that the model compound, 2,2-dinitropropane, was converted completely to 2-nitropropane with BNAH in dimethylformamide or acetonitrile under sunlamp irradiation for 16 h.

Tributyltin hydride in refluxing benzene with benzoyl peroxide initiator was also reported[15] to convert simple *tert*-nitroalkanes to hydrocarbons. This

reagent was found here to give 2-nitropropane from 2,2-dinitropropane in only 9% conversion after 15 h of irradiation.

The reaction of HNDZ with BNAH was much more rapid than that of 2,2-dinitropropane, reaching completion with only room light in minutes. Extraneous NMR peaks of the product suggested that nitramino, as well as *gem*-dinitro, groups were reduced. Using 3-nitraza-1,5-diaminopentane dihydrochloride as an available model compound confirmed that nitramino groups are reduced under these conditions; diethylenetriamine dihydrochloride, characterized by its previously reported NMR spectrum,[16] was the sole product. Denitration of a secondary nitramine by tributyltin hydride, initiated by azoisobutyronitrile, has been reported.[17]

As an alternative to Mannich reactions and selective reductions, another route was pursued involving 1,5-dialkyloctahydro-3,7-bis(methylene)-1,5-diazocines[8] as intermediates. Thus, displacements of 3-chloro-2-chloromethylpropene with iodide and benzylamine, respectively, gave 3-iodo-2-iodomethylpropene[18] and *N,N'*-dibenzyl-2-methylene-1,3-propanediamine.[8] The alkylation reaction between these intermediates gave 1,5-dibenzyloctahydro-3,7-bis-(methylene)-1,5-diazocine.



Debenzylation of the latter compound by hydrogenolysis with Pearlman's catalyst in acetic anhydride resulted in significant decomposition with no appreciable yield of desired product. When the hydrogenolysis was repeated with methanol solvent and two equivalents of hydrogen, the double bonds were reduced, with no debenzylation. The reagent α-chloroethyl chloroformate (ACE-Cl) has been utilized for various *N*-dealkylations of tertiary amines[19] via decarboxylation of relatively unstable 1-chloroethyl carbamate intermediates. The debenzylation of 1,5-dibenzyloctahydro-3,7-bis(methylene)-1,5-diazocine with this reagent gave the secondary amine dihydrochloride in 52% yield.

Acetylation of this diamine with acetic anhydride in aqueous potassium carbonate gave the corresponding bisacetamide quantitatively. Cis and trans

rotamers of the bisacetamide are distinguishable by ^{1}H and ^{13}C NMR because of hindered rotation about the C-N bond of amides.[20]

Ozonolysis of the bisacetamide in methanol at -72 °C, followed by reductive workup with dimethyl sulfide,[21] gave 1,5-diacetyltetrahydro-1,5-diazocine-3,7(2*H*,6*H*)-dione in 59% yield. Aqueous workup[22] gave low recovery, and NMR evidence suggested the formation of a soluble hydrate.

Although oximation of this dione did not take place in aqueous ethanol, hydroxylamine hydrochloride in pyridine-ethanol gave the dioxime in 90% yield. Because of the asymmetry of the hydroximino groups, and the syn and anti isomerism about the amide groups, the ^{1}H and ^{13}C NMR spectra of the dioxime are complex (five geometric isomers).

Application of reported oxime-to-nitro conversion conditions,[23] involving reaction of the oxime with chlorine gas followed by ozonization, failed to give the *gem*-chloronitro derivative. An oxime to *gem*-dinitro conversion has been reported by Bull, Jones, and Meakins,[24] involving nitration (by nitric acid in dichloromethane) followed by oxidation of *gem*-nitronitroso to *gem*-dinitro by hydrogen peroxide. Under these conditions, the dioxime gave a bicyclic product resulting from transannular bridging. A similar bridging, also giving fused five-membered rings, was reported by Paquette[25] for [4]peristylane derivatives. However, nitration with an equimolar mixture of ammonium nitrate and 100% nitric acid resulted in conversion of the [4]peristylanedione dioxime to the *gem*-dinitro-substituted monoketone in addition to the undesired bridging product.[25c] Room-temperature nitration of the diazocine dioxime with HNO_3-NH_4NO_3 yielded a product mixture which appeared complex by ^{1}H and ^{13}C NMR due mainly to the syn-anti isomerism induced by the *N*-acetyl substit-

uents. Resolution of the reaction products by chromatography is under investigation. Attempts to nitrolyze the crude amide mixture were unsuccessful.

Another target of this investigation was 1,1-bis(difluoramino)-3,3-dinitrocyclobutane. Under an earlier ONR-supported program, 1,1,3,3-tetranitrocyclobutane[26] was synthesized, and the chemistry developed is potentially applicable to the NF_2 analogue. 1-Amino-3,3-dinitrocyclobutane, available from that program, was transformed into the alcohol via diazotization with sodium nitrite in acetic acid. Attempts were made to oxidize this alcohol to the ketone using pyridinium chlorochromate, chromic acid in acetic acid at 35-70°C, aqueous chromic acid at 40-80°C, and chromium trioxide in refluxing acetone. In all of these cases, the alcohol proved resistant to oxidation. Swern oxidation (oxalyl chloride-dimethyl sulfoxide) also did not give a significant amount of ketone, although traces of ketonic product were observed in the infrared spectrum.

Brief attempts were also made to synthesize 3,3-bis(difluoramino)-1,5,5-trinitropiperidine. The all-nitro analogue, 1,3,3,5,5-pentanitropiperidine, has been reported,[12,27] offering a standard for comparison of properties. The reported synthesis of 1-acetyl-3,5-piperidinedione[28] was repeated, but an attempted acetylation of the precursor, 3,5-piperidinedione hydrochloride, appeared to yield the *O*-acetylated enol acetate.

EXPERIMENTAL

2-Bromo-*N,N'*-di-*tert*-butyl-2-nitro-1,3-propanediamine. A solution of 2-bromo-2-nitro-1,3-propanediol (25.0 g, 0.125 mol) and *t*-butylamine (18.3 g, 0.250 mol) in 100 mL 1,1,2-trichlorotrifluoroethane (Freon-113) was stirred for 2 days at ambient temperature. Chloroform (50 mL) was added and the solution was washed with water (50 mL), dried ($MgSO_4$), and stripped of solvents by rotary evaporation under vacuum to yield 34.4 g (89%) of 2-bromo-*N,N'*-di-*tert*-butyl-2-nitro-1,3-propanediamine; mp (DSC) 62°C, dec >120°C; ^{1}H NMR (DMSO-d_6) δ 1.00 (s, CH_3), 1.84 (NH), 3.25, 3.35 (2 d, AB pattern, CH_2); ^{1}H NMR ($CDCl_3$) δ 1.07 (s, CH_3), 1.26 (NH), 3.41, 3.42 (2 d, AB pattern, CH_2); ^{13}C NMR (DMSO-d_6) δ 28.5 (CH_3), 49.9 (CMe_3 and CH_2), 103.5 ($CBrNO_2$); ^{13}C NMR (DMSO-d_6-$CDCl_3$ 1:1) δ 28.4 (CH_3), 49.6 (CH_2), 49.7 (CMe_3), 101.6 ($CBrNO_2$). Anal. Calcd. for $C_{11}H_{24}BrN_3O_2$: C, 42.59; H, 7.80; N, 13.54. Found: C, 42.92; H, 7.90; N, 13.59.

5-Bromo-1,3-di-*tert*-butylhexahydro-5-nitropyrimidine. A solution of 2-bromo-*N,N'*-di-*tert*-butyl-2-nitro-1,3-propanediamine (3.708 g, 11.95 mmol) and paraformaldehyde (0.362 g, 12.04 mmol) in 400 mL methanol was stirred at room temperature for 3 days. The solution was filtered and methanol was removed by rotary evaporation. The residue was dissolved in chloroform (300 mL), extracted with water (100 mL), and dried ($MgSO_4$). The chloroform was removed by rotary evaporation, and the residue was recrystallized from 150 mL of petroleum ether-dichloromethane (10:1) to yield 2.86 g (74%) 5-bromo-1,3-di-*tert*-butylhexahydro-5-nitropyrimidine; mp (DSC) 76°C (dec); ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 18 H, CH_3), 2.70, 2.78 (2 d, AB pattern, J = 12.2 Hz, 9.1 Hz,

3 H), 4.14 (d, J = 12.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 26.3 (CH_3), 53.8 (CMe_3), 56.0 (CH_2CBrNO_2), 63.2 (NCH_2N), 86.8 ($CBrNO_2$); IR (neat) $_{as}(NO_2)$ 1560 cm^{-1}. Anal. Calcd. for $C_{12}H_{24}BrN_3O_2$: C, 44.73; H, 7.51; Br, 24.80; N, 13.04; O, 9.93. Found: C, 45.40; H, 7.61; Br, 24.16; N, 12.86; O (by difference), 9.97.

5-Bromohexahydro-1,3,5-trinitropyrimidine. 5-Bromo-1,3-di-*tert*-butylhexahydro-5-nitropyrimidine (0.8965 g, 2.78 mmol) was added portionwise, with stirring, to 100% HNO_3 (35 mL, 0.83 mol), cooled in an ice-ethanol bath. The mixture was stirred at ambient temperature overnight and was then quenched with ice. The product was extracted with dichloromethane, dried ($MgSO_4$), and recrystallized (CH_2Cl_2-$CHCl_3$), to yield 0.3606 g (43%) of 5-bromohexahydro-1,3,5-trinitropyrimidine; mp (DSC) 155°C; ^1H NMR (acetone-d_6) δ 5.03, 5.42 (2 d, AB pattern, $^2J_{HH}$ = 15.6 Hz, 4 H), 6.13, 6.31 (2 d, AB, J = 14.9 Hz, 2 H); ^{13}C NMR (acetone-d_6) δ 55.3 (CH_2CBrNO_2), 60.4 (NCH_2N), 83.2 ($CBrNO_2$). Anal. Calcd. for $C_4H_6BrN_5O_6$: C, 16.01; H, 2.02; N, 23.34. Found: C, 16.13; H, 1.94; N, 22.95.

Reaction of *N*-Benzyl-1,4-dihydronicotinamide (BNAH) with 2,2-Dinitropropane. 2,2-Dinitropropane (13.5 mg, 0.101 mmol) and BNAH (54.5 mg, 0.254 mmol, Tokyo Kasei) were dissolved in 0.5 mL CD_3CN in a 5-mm NMR tube. The solution was purged with nitrogen and irradiated with a 275-W sunlamp for 16 h. The ^1H NMR spectrum showed essentially complete conversion of 2,2-dinitropropane to 2-nitropropane. A similar conversion was observed in dimethylformamide-d_7 with 20.5 h irradiation.

Reaction of *N*-Benzyl-1,4-dihydronicotinamide (BNAH) with 3-Nitraza-1,5-diaminopentane Dihydrochloride (XIII-diamine Dihydrochloride). A solution of 3-nitraza-1,5-diaminopentane dihydrochloride (XIII-diamine dihydrochloride)[29] (22.6 mg, 0.102 mmol) and BNAH (22.9 mg, 0.107 mmol) in 0.5 mL dimethylform-

amide-d_7 and 0.5 mL D_2O in a 5-mm NMR tube was purged with nitrogen and irradiated with a 275-W sunlamp for 18 h. The ^1H NMR spectrum showed 74% conversion of XIII-diamine dihydrochloride to diethylenetriamine dihydrochloride.[16]

3-Iodo-2-iodomethylpropene.[18] To a stirred suspension of sodium iodide (607.2 g, 4.05 mol) in 1.25 L of refluxing acetone was slowly added 3-chloro-2-chloromethylpropene (250.5 g, 2.00 mol). The mixture was refluxed for 8 h and then stirred at ambient temperature overnight. Solids were filtered off and acetone was removed from the solution by rotary evaporation. The product was washed with 500 mL of saturated aqueous sodium thiosulfate. The lower layer was removed and the aqueous layer was extracted with pentane (500 mL). The combined organic phases were dried (Na_2SO_4) and solvent was removed by rotary evaporation. The residue was crystallized from cold methanol (175 mL); concentration of the mother liquor and recrystallization yielded a second crop, giving a total of 533.6 g (86%) of 3-iodo-2-iodomethylpropene: ^1H NMR ($CDCl_3$) δ 4.13 (s, CH_2I), 5.35 (s, $=CH_2$); ^{13}C NMR ($CDCl_3$) δ 6.7 (CH_2I), 116.2 ($=CH_2$), 143.8 ($C=CH_2$).

***N,N'*-Dibenzyl-2-methylene-1,3-propanediamine.** The procedure used is a modification of that reported for other *N,N'*-dialkyl derivatives.[8] To benzylamine (1025 mL, 10.0 mol), initially at 40°C, was added 3-chloro-2-chloromethylpropene (251.4 g, 2.01 mol) dropwise over 8 h at 60-73°C. The mixture was then stirred at ambient temperature for 16 h, and suspended benzylamine hydrochloride was filtered off. After 24 h, more benzylamine hydrochloride was filtered off, and excess benzylamine was distilled off under vacuum. Addition of 1 L of 2-propanol to the viscous residue precipitated more benzyl-

amine hydrochloride, which was filtered off and washed with carbon tetrachloride. Solvents were removed by rotary evaporation under reduced pressure, and additional benzylamine hydrochloride was filtered off to yield 499.1 g (93%) of *N,N'*-dibenzyl-2-methylene-1,3-propanediamine as a viscous, red-orange oil: bp 163°C (0.025 torr); ^{1}H NMR ($CDCl_3$) δ 1.40 (s, NH), 3.17 (s, 1,3-CH_2), 3.60 (s, CH_2Ph), 4.99 (s, $=CH_2$), 7.11-7.24 (C_6H_5); ^{13}C NMR ($CDCl_3$) δ 52.1, 52.4 (CH_2's), 111.2 ($=CH_2$), 126.0 (phenyl-C_4), 127.3 (phenyl-C_2), 127.5 (phenyl-C_3), 139.8 (phenyl-C_1), 145.4 ($C=CH_2$).

1,5-Dibenzyloctahydro-3,7-bis(methylene)-1,5-diazocine.[8] Solutions of 3-iodo-2-iodomethylpropene (40.0 g, 0.150 mol) in 250 mL absolute ethanol and of *N,N'*-dibenzyl-2-methylene-1,3-propanediamine (46.0 g, 0.149 mol) in 250 mL ethanol were added simultaneously, dropwise, over 2 h, to a suspension of potassium carbonate (45.6 g, 0.330 mol) in 250 mL of absolute ethanol. The solution was refluxed for 5.5 h and then was stirred at ambient temperature overnight. The ethanolic solution was filtered and ethanol was removed by rotary evaporation. The residue was dissolved in dichloromethane, the solution was filtered, and then dichloromethane was removed by rotary evaporation. Dissolution in methanol removed a small quantity of insoluble impurities; then methanol was removed by rotary evaporation, leaving 47.7 g of 1,5-dibenzyl-octahydro-3,7-bis(methylene)-1,5-diazocine as a reddish, viscous oily product, 76-77% pure by ^{1}H NMR integrations: ^{1}H NMR ($CDCl_3$) δ 3.26 (s, 8 H, $-CH_2C=$), 3.64 (s, 4 H, CH_2Ph), 4.82 (s, 4 H, $=CH_2$), 7.24-7.37 (m, 10 H, C_6H_5); ^{13}C NMR (CD_3OD-$CDCl_3$ 5:1) δ 59.7 (CH_2Ph), 60.4 ($-CH_2C=$), 115.0 ($=CH_2$), 127.8 (phenyl-C_4), 129.1, 129.9 (phenyl-C_2,C_3), 140.2 (phenyl-C_1), 145.7 ($C=CH_2$).

Octahydro-3,7-bis(methylene)-1,5-diazocine Dihydrochloride. Crude 1,5-dibenzyloctahydro-3,7-bis(methylene)-1,5-diazocine (46.7 g, 0.147 mol) in 250 mL dichloroethane was cooled to 2-3 °C in an ice-water bath, and 1-chloroethyl chloroformate (50 mL, 0.463 mol) was added dropwise over 30 min. The solution was heated at reflux for 1.5 h, and then the 1,2-dichloroethane was removed by rotary evaporation under reduced pressure. Methanol (250 mL) was added, and the solution was refluxed for 1.3 h. This solution was concentrated to half its original volume by rotary evaporation. At room temperature, white microcrystals precipitated, which were filtered off, washed with methanol, and vacuum-dried to yield 12.2 g (52% based on pure octahydro-3,7-bis(methylene)-1,5-diazocine dihydrochloride): mp (DSC) 250°C (dec); ^{1}H NMR (D_2O) δ 3.94 (s, NCH_2C), 4.83 (s, NH), 5.80 (s, $=CH_2$); ^{13}C NMR (D_2O) δ (vs. sodium trimethylsilylpropionate-d_4) 51.9 (NCH_2C), 132.6 ($=CH_2$), 134.9 ($C=CH_2$). Anal. Calcd. for $C_8H_{16}N_2Cl_2$: C, 45.51; H, 7.64; N, 13.27. Found: C, 45.51; H, 7.49; N, 13.06.

1,5-Diacetyloctahydro-3,7-bis(methylene)-1,5-diazocine. Acetic anhydride (23.2 g, 0.208 mol) was added dropwise over 30 min with vigorous stirring to a solution of octahydro-3,7-bis(methylene)-1,5-diazocine dihydrochloride (11.0 g, 0.0521 mol) and potassium carbonate (15.7 g, 0.104 mol) in 300 mL H_2O. The solution was stirred for 3 days and then was extracted with dichloromethane (6 x 300 mL). Solvent was removed and the yellowish liquid residue was passed through silica gel with 300 mL CH_2Cl_2; the effluent was dried ($MgSO_4$) and concentrated by rotary evaporation to yield 11.6 g (100%) of 1,5-diacetyloctahydro-3,7-bis(methylene)-1,5-diazocine. After 8 days, the product crystallized: mp (DSC) 92°C. *cis*-1,5-Diacetyloctahydro-3,7-bis(methylene)-1,5-diazocine: ^{1}H NMR ($CDCl_3$) δ 2.09 (s, CH_3), 3.97 (s, anti N-CH_2), 4.10 (s, syn N-CH_2), 5.32

(s, anti C=CH_2), 5.41 (s, syn C=CH_2); ^{13}C NMR ($CDCl_3$) δ 21.7 (CH_3), 51.6 (anti N-CH_2), 51.8 (syn N-CH_2), 115.7 (anti C=*C*H_2), 121.3 (syn C=*C*H_2), 141.5 (anti *C*=CH_2), 142.3 (syn *C*=CH_2), 170.8 (C=O). *trans*-1,5-Diacetyloctahydro-3,7-bis-(methylene)-1,5-diazocine: ^1H NMR ($CDCl_3$) δ 2.09 (s, CH_3), 4.02 (s, anti N-CH_2), 4.13 (s, syn N-CH_2), 5.19 (s, C=CH_2); ^{13}C NMR ($CDCl_3$) δ 21.6 (CH_3), 50.3 (anti N-CH_2), 54.2 (syn N-CH_2), 118.6 (C=*C*H_2), 140.7 (*C*=CH_2), 170.6 (C=O). NMR analysis showed a ratio of 42:58 for cis:trans isomers. Anal. Calcd. for $C_{12}H_{18}N_2O_2$: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.75; H, 7.96; N, 12.50.

1,5-Diacetyltetrahydro-1,5-diazocine-3,7(2*H*,6*H*)-dione. A solution of 1,5-diacetyloctahydro-3,7-bis(methylene)-1,5-diazocine (0.5178 g, 2.33 mmol) in 50 mL methanol at -72 °C was purged with oxygen and then was sparged with ozone generated by a Welsbach T-23 ozonator (4 psig, 0.020 SCFH) for 15 min. The solution, blue from dissolved ozone, was purged with oxygen for another 45 min. The cooling bath was removed, O_2 purging continued for another 15 min, and then 2.0 mL of a methanolic solution containing 0.4 mL (5.4 mmol) of dimethyl sulfide was added. The suspension was recooled with dry ice and product was removed by filtration. The methanol solvent was removed by rotary evaporation, and the residual viscous, light yellow oil was evacuated overnight to remove dimethyl sulfoxide byproduct. Recrystallization of the residue from 20 mL of methanol-ethanol (1:1) yielded a second crop. A third crop was obtained by evaporation of the alcohol solvent, dissolution of residual solid in water, evaporation of excess water, dehydration of the glassy solid by heating (>100°C) under vacuum, and recrystallizing the crystalline residue twice from methanol. The total yield of 1,5-diacetyltetrahydro-1,5-diazocine-3,7(2*H*,6*H*)-dione was 0.3084 g (59%): mp (DSC) 249°C. *cis*-1,5-Di-

acetyltetrahydro-1,5-diazocine-3,7(2*H*,6*H*)-dione: ^{1}H NMR (DMSO-d_6) δ 1.94 (s, CH_3), 3.88 (s, anti N-CH_2), 4.21 (s, syn N-CH_2); ^{13}C NMR (DMSO-d_6) δ 21.1 (CH_3), 58.8 (anti N-CH_2), 59.6 (syn N-CH_2), 171.29 (CH_3C=O), 205.6 (anti CH_2C=O), 208.0 (syn CH_2C=O). *trans*-1,5-Diacetyltetrahydro-1,5-diazocine-3,7(2*H*,6*H*)-dione: ^{1}H NMR (DMSO-d_6) δ 1.91 (s, CH_3), 4.16 (s, anti N-CH_2), 4.46 (s, syn N-CH_2); ^{13}C NMR (DMSO-d_6) δ 21.0 (CH_3), 58.4 (anti N-CH_2), 60.1 (syn N-CH_2), 171.32 (CH_3C=O), 207.1 (CH_2C=O). NMR analysis showed a ratio of 52:48 for cis:trans isomers. Anal. Calcd. for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.24; N, 12.38. Found: C, 52.71; H, 6.39; N, 12.30.

1,5-Diacetyltetrahydro-1,5-diazocine-3,7(2*H*,6*H*)-dione Dioxime. A solution of 1,5-diacetyltetrahydro-1,5-diazocine-3,7(2*H*,6*H*)-dione (0.101 g, 0.445 mmol) and hydroxylamine hydrochloride (0.218 g, 3.14 mmol) in 2.0 mL of pyridine and 2.0 mL of ethanol was refluxed for 2 h and then stored in a freezer overnight. The white precipitate was collected and solvents were removed from the filtrate under vacuum. Water was added to the residue, giving a white solid, which was vacuum-dried over P_4O_{10}; the total yield of 1,5-diacetyltetrahydro-1,5-diazocine-3,7(2*H*,6*H*)-dione dioxime was 0.103 g (90%): mp (DSC) 247°C (dec). ^{1}H and ^{13}C NMR analyses showed peaks corresponding to all five possible cis and trans diacetyl and cis and trans dioxime geometric isomers (including *syn* and *anti trans-(E),(E)* isomers), but assignments were not made to individual isomers. ^{1}H NMR (DMSO-d_6) δ 1.95-1.99 (CH_3, 4 peaks resolved out of 8 possible), 3.88-4.45 (N-CH_2, 14 peaks resolved out of 16 possible), 10.75, 10.85, 11.03, 11.04, 11.07, 11.13, 11.29, 11.33 (NOH, 8 peaks resolved out of 8 possible); ^{13}C NMR (DMSO-d_6) δ 20.8-21.8 (CH_3, 7 peaks resolved out of 8 possible), 44.6-52.7 (N-CH_2, 12 peaks resolved out of 16

possible), 153.1, 153.8, 154.0, 154.1, 154.5, 154.6, 155.0, 155.7 (C=NOH, 8 peaks resolved out of 8 possible), 169.4-171.0 (C=O, 5 peaks resolved out of 8 possible). Anal. Calcd. for $C_{10}H_{16}N_4O_4$: C, 46.87; H, 6.29; N, 21.86. Found: C, 47.24; H, 6.38; N, 22.08.

2,5-Diacetyloctahydro-3a,6a-dinitropyrrolo[3,4-*c*]pyrrole. The dioxime (0.172 g, 0.672 mmol) was suspended in 6 mL of dichloromethane and cooled to -5°C, and 100% HNO_3 (1.00 mL) was added dropwise with stirring over 5 min. The solution stirred for 20 min at -5°C and 1 h at 15 °C. Hydrogen peroxide (30%, 1.0 mL) was added and washed in with 1.0 mL CH_2Cl_2; the solution was stirred (20 min) until it became colorless. Anhydrous sodium sulfate (6 g) was added, and the suspension was stirred overnight. Sodium sulfate was filtered off, CH_2Cl_2 was removed under vacuum, and the residual off-white solid was recrystallized from chloroform-heptane (1:1), giving 0.0814 g (42%) of 2,5-diacetyloctahydro-3a,6a-dinitropyrrolo[3,4-*c*]pyrrole as white fluffy crystals: mp (DSC) 162°C; ^{1}H NMR (DMSO-d_6) δ 2.02 (CH_3), 4.07-4.63 (m, 2 AB patterns, CH_2); ^{13}C NMR (DMSO-d_6) δ 21.4 (CH_3), 52.4, 52.5, 52.8 (syn and anti CH_2), 93.4, 94.6, 95.8 (syn and anti CNO_2), 168.65, 168.72 (cis and trans isomers C=O); IR (CH_2Cl_2) $_{as}(NO_2)$ 1564 cm^{-1}. Anal. Calcd. for $C_{10}H_4N_4O_6$: C, 41.96; H, 4.93; N, 19.57. Found: C, 41.69; H, 4.97; N, 19.23.

3,3-Dinitrocyclobutanol. A solution of sodium nitrite (9.0 g, 130 mmol) in water (15 mL) was added dropwise to a suspension of 3,3-dinitrocyclobutylamine hydrochloride[26] (5.0 g, 25 mmol) in 9% aqueous acetic acid (100 mL) at 5°C. The mixture was stirred at 5°C for 2 h and then allowed to warm to room temperature over 1 h. The mixture was stirred at room temperature for 11 h and was extracted with diethyl ether. The ethereal extracts were combined,

washed with water, 10% aqueous $NaHCO_3$, and brine (2x). The organic layer was dried ($MgSO_4$) and the solvent was removed under vacuum. The residual oil was dissolved in methanol (20 mL) and treated with 5 drops conc. HCl. The mixture was stirred at room temperature for 16 h. The solvent was removed under vacuum, and the residue was dissolved in dichloromethane. This solution was washed with water, aqueous $NaHCO_3$, and brine, and then dried ($MgSO_4$) and concentrated under reduced pressure to give 3.3 g of an oil. GLC analysis revealed three components, 3,3-dinitrocyclobutanol (85% pure, 68% yield), 1-chloro-3,3-dinitrocyclobutane, and 3,3-dinitrocyclobutane. Acetic anhydride and triethylamine were added to a solution of the crude 3,3-dinitrocyclobutanol (85% pure, 200 mg) in dichloromethane, and the solution was stirred at room temperature for 16 h. Solvent was evaporated, and the residue was chromatographed on silica gel (70% dichloromethane-hexane) to give 162 mg (76%) of 1-acetoxy-3,3-dinitrocyclobutane: ^1H NMR ($CDCl_3$) δ 2.02 (s, 3 H, CH_3), 3.09-3.31 (dd, 2 H, CH_2), 3.43-3.59 (dd, 2 H, CH_2), 5.09 (quint, 1 H, CH); IR (neat) 1580, 1735, 2975 cm^{-1}. The acetate ester (127 mg, 0.62 mmol) was dissolved in 5 mL of methanol containing 0.5 mL conc. HCl, stirred at room temperature for 14 h, and then heated under reflux for an additional 1 h. The solvent was removed under vacuum, and the residue was dissolved in CH_2Cl_2. This solution was washed with water, aqueous $NaHCO_3$, and brine, and then dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give 89 mg (88%) of a yellow oil. GLC analysis showed it to be 95-96% pure 3,3-dinitrocyclobutanol, contaminated by 1-chloro-3,3-dinitrocyclobutane; ^1H NMR ($CDCl_3$) δ 3.16-3.19 (m, 2 H, CH_2), 3.43-3.50 (m, 2 H, CH_2), 4.62 (quint, 1 H, CH); IR (neat) 1570, 3000, 3450 cm^{-1}.

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